Combinatorial Synthesis and Analysis for Electronic Materials

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Abstract

Combinatorial Synthesis and Analysis for Electronic Materials. JEFF KIEFT (Colorado School of Mines, Golden, CO 80401 USA) DR. DAVID GINLEY (National Center for Photovoltaics, National Renewable Energy Laboratory, Golden, CO 80401).

Optimizing material opto-electronic properties will benefit markets such as solar cells, Flat Panel Displays (FPDs), and electrochromic windows. Better n- and p-type Transparent Conducting Oxides (TCOs for p-n heterojunctions or homojunctions in these applications are being actively pursued. Identifying candidate materials and optimal compositions is a complex task. An efficient path toward optimization is by a combinatorial or parallel experimentation approach. By applying the combinatorial approach to rf magnetron sputtering using multiple targets, compositional gradients across the substrate can be achieved. A compositional library containing the informational equivalent of many linear experiments, is contained in a single deposition. Techniques such as Hall and Seebeck methods, can be used to provide electrical properties. By scanning samples with tools such as a UV/Vis real-time spectrophotometer interfaced with a graphical analysis package, desired optical properties can be linked with precise compositions not only for p-type TCOs but also for electronic material systems.

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Introduction

TCO Background

Transition metal oxides have attracted interest at the National Renewable Energy Laboratory (NREL) due to their structural tolerance to oxygen defects, i.e., oxygen vacancies and interstitials. These materials are under research at NREL for use in batteries, photovoltaics, ferroelectrics, and transparent conductors. As one of the subsets of transition metal oxides, thin film Transparent Conducting Oxides (TCOs), have attracted attention since Badeker discovered the first TCO, CdO, in 1907 (1). Today TCOs are used in solar cells (diodes), flat panel displays (FPDs), electrochromic windows, current injection lasers, light-emitting diodes (LEDs),and gas sensors to name only a few applications.

TCOs, in addition to their structural tolerance as oxides, are employed for their conduction and transparency. Through the presence of natural defects (usually oxygen vacancies) and the addition of dopants, the TCOs are made conductive. Oxides have been the material of choice due to the large dc electrical conductivities. n-type oxides, for instance, have conductivities of approximately 1000 S cm^{-1} (2). Once their conductivities become comparable to those found in n-type materials, p-type materials have potential uses in p-n heterojunctions and in homojunctions. Without doping, however, oxides such as ZnO have wide bandgaps and are insulators. Depending on many factors including the dopant, some materials including ZnO can be made both p- and n-type. Whether a material is p- or n-type, conductivity is directly related to transparency. If the TCO is too conductive—more like a metal—then there are too many electrons and transparency will be reduced because the "electron gas" reflects/absorbs light. In order for a TCO to be transparent in the visible wavelength range of light, the bandgap must be greater than ~3 eV or ~380 nanometers. This is above the energy range of visible light. Carriers can be excited by light above and below the energy range of visible light and still remain transparent in the visible part of the spectrum. In other words, there is a transparent window in the visible range between the band edge and the plasma edge. The band edge must be greater than ~3 eV and the plasma edge must be less than ~1.7eV for transparency in the visible spectrum. This window corresponds to the ~400 to 700 nanometer wavelengths of light.

The plasma frequency (ω_p) is related to the square root of the carrier concentration (N) as seen in the following equation (3) :

$$\omega_p = \left(\frac{4 \pi N q^2}{m^* \varepsilon} \right)^{\frac{1}{2}}$$

The reader is referred to Pankove's book for further description of this equation, but relationship between plasma frequency and carrier concentration is easily seen. Because a smaller carrier concentration (N) results from lower energy light, many carriers have not been energized to the conduction band. Then the plasma edge remains below the visible energy range of light and the film will be transparent to the eye.

The path to conduction is a tradeoff between mobility and carrier conduction. Desired mobility and carrier concentration are on the order of tens of $cm^2 V^{-1} s^{-1}$ and $10^{21} cm^{-3}$ respectively. These values compare to well-known doped n-type semiconductors such as indium tin oxide (ITO). The mobility value is, however, more important than the value of carrier concentration because the charge carriers must be mobile in order to achieve conduction. A useful TCO then, balances the transparency with conduction (4).

The Combinatorial Approach

What is the combinatorial approach to experimentation and why do it? "Combinatorial" refers to parallel experimentation. It refers to simultaneous, compositionally-graded deposition from multiple sources and the associated analytical system to extract opto-electric property values (figure 1). As mentioned above, pin-pointing desired TCO composition and properties is a balancing act which may become even more difficult as more complex materials are explored. With the use of ternary and quaternary material systems, phase space becomes increasingly difficult to control and analyze. At NREL, a combinatorial system is being assembled to study several renewable energy projects. A-Si systems, lithium battery chemistry, and TCOs are among the projects which could benefit from the combinatorial approach. Some of these efforts explore ternary, quaternary and even more complex phase space. A-Si solar cells use ternary layers (Si, H, B, and Si, Ge, H); a recent lithium battery electrode utilized $LiCo_{1-z-x}Ni_zMn_xO_y$ (5); TCOs being looked at include the study of oxygen vacancies in ZnO: Al through control of the oxygen partial pressure, potassium doping of $SrCu_2O_2$ and doping of $CuAlO_2$ in order to improve conductivity. Adding an annealing step to any of these projects increases the complexity and variable interdependence. Sample deposition by sputtering, for instance, might begin with two or three binary material targets. One or more of these targets would be positioned at an angle to the substrate so as to deposit a material gradient (figure 2). Adding a reactive gas and substrate heating during analysis and the phase space would become at least four-dimensional. In order to extract the data from this deposited "library," real-time analysis and fast scanning are necessities. The desired optical properties may be calculated by such tools as a near-real-time spectrophotometer or slightly slower scanning Raman measurement. By using a broadband spectrophotometer, full spectral measurements of the entire compositional library (sample) can be taken in short order. The large amount of data generated by a broadband spectrophotometer, can be stored and analyzed quickly with the proper setup. If spectra can be downloaded to a graphical analysis package, sample parameters can be determined. For example, adjacent fringe maxima in a transmission spectrum (figure 3) can be used to calculate thickness using the simple equation (3):

$$n = \frac{1}{\left(\frac{1}{\lambda_2} - \frac{1}{\lambda_1}\right)x}$$

The combinatorial approach offers much potential time savings over a linear approach in terms of the number of experiments which must be performed. Data collection and analysis must be organized and rapid to facilitate interpretation of hundreds of thousands of data points. Subsequent sputter deposition can then narrow in on the optimal compositional range.

TCO Deposition Techniques

As one of the reasons for the need for the combinatorial synthesis and analysis, deposition techniques and conditions have a large effect on material properties and compositions (6). Two possible methods for TCO deposition are PLD and rf magnetron sputtering. PLD employs high energy (terawatts) pulses to dislodge atoms from targets. The high energy pulses eject atoms from the target without regard for their atomic weight. The thin films are of the same stoichiometry as the targets. $CuAlO_2$ made at NREL was PLD deposited (7). PLD is capable of multi-target use, but pulses must alternate between targets. If two target materials analogously called swiss and cheddar are to be deposited, the swiss/cheddar cheese will be nearly homogeneous due to alternating monolayer depositions which we "melted" together (8). Sputtering, on the other hand, can simultaneously deposit from multiple targets. A plasma can be employed for reactive chemistry and deposition of reactive intermediates in both PLD and rf sputtering. Sputtering is considered the cheaper method and is easily scaled up and used by industry. It is useful for coating large areas of glass, i.e. architectural glass, relatively uniformly. Multiple targets can provide a uniform gradient. Conformal coating or coating of non-uniform surfaces is an added benefit of sputtering. Control of the composition, however, is somewhat imprecise.

In sputtering materials, Rf cycling rather than dc is used because of the charge buildup which accompanies a poorly conducting target (insulators). The cycling of the target and substrate from cathode and anode occurs at the radio frequency of 13.56 MHz so that the ions and electrons alike present in the plasma are pulled to the target (9,10,11). In order to increase sputter yields, magnetrons that produce an electric field near the targets are used to confine the plasma. Argon ions are then attracted to the targets in a pattern based on magnets placed below the targets. The gas ions hit the targets with enough force to eject target atoms. Energy is not high enough to eject target atoms without regard to molecular weight so the stoichiometry at the substrate will not exactly match that at the target. Rf sputtering will produce lower yields than dc sputtering because of heat/resistance generated at the target and because some power is reflected (unused) in rf despite impedance matching.

The plasma, or mix of electrons and ions, must be controlled in order to balance the Mean Free Path (MFP) with the number of gas ions. If the gas pressure is too high, the MFP is low and little deposition occurs. If gas pressure is too low, little ionization occurs and little deposition occurs (9). A difficulty in rf magnetron sputtering is control of composition. The ratio of codopants for instance is only roughly controllable by gas pressure and target power.

Materials and Methods

As a result of our efforts, the rf magnetron sputtering system and planning the characterization setup are nearly complete. However, first deposition has not yet been achieved. Thus the following details pertain to expected materials and methods.

The RF Magnetron Sputtering System

Cooling, gas, and vacuum systems (figure 4), all of which include safety features, have been installed. Assembly of the rf magnetron sputtering system began with a Perkin- Elmer fifteen inch diameter stainless steel chamber resurrected after previous sputtering incarnations. Part of the vacuum system, the cryo-chamber was attached below the main chamber in order to adsorb gases which fall to the bottom due to the 15 to 20K temperature in the cryopump itself. An MDC gate which operates by nitrogen gas, separates the chamber from the cryochamber. Nitrogen gas was used to operate the gate valve because the central compressed air supply was contaminated with water and oil. A Huntington screw valve separates the rough lines from the cryo lines so that the cryochamber can be regenerated separately from the chamber.

Not only is cooling water necessary for the annealing furnace to be used following deposition, but it is also essential for both the targets and the compressor. Two copper pipe water manifolds were fabricated to transport coolant from the central building lines and to split the water to the three possible targets at the chamber. A simple cartridge filter placed ahead of the first manifold will maintain ion-free coolant to prevent arcing and water deposits at the target magnets. In-line solenoids will shut off the water supply in the event of a water leak. Water flow gauges just ahead of the targets will shut off the targets in case the water pressure drops to less than one-half gallon per minute to each target.

A gas manifold to control nitrogen, argon, nitrous oxide, or oxygen input to the chamber was built from quarter-inch stainless steel tubing with Swagelok fittings. MKS mass flow controllers (MFCs) were placed in-line in order to control the volume of gas input. Nitrogen is run through the 100 sccm MFC and oxygen is run through the 20 sccm MFC because of the larger molecular size of nitrogen. Nitrogen is also expected to be used in larger quantities. The nitrogen MFC can be bypassed in order to purge the chamber with nitrogen. With this setup, two gases can be fed simultaneously. The gases run from their cylinders to the manifold through quarter-inch polyethylene tubing. The nitrogen supply for the gate valve is run through eighth-inch nylon tubing since only a small amount (pulse) of gas is needed to open or close the valve.

There are three sputter guns. One two-inch gun faces the substrate directly. Two one-inch guns on either side of the two-inch gun allow for two compositional gradients. A Dressler RF Power Generator supplies 13.56 MHz. Manitou Systems, Inc. impedance matching network maintains efficient power usage. Two Granville Phillips Convectron gauges measure the pressure both inside the chamber and inside the cryochamber. An MKS Barytron pressure transducer also measures the chamber pressure. Multiple pressure gauges are needed because each operates on a different principle and measures a different range of pressures. A Balzers TPG200 "rough gauge" measures pressure in the rough pump range. It indicates when the rough pump should be switched off and the cryopump should be switched on. [refer to system diagram] When the rough pump is switched off, an ASCO Red Hat vacuum release valve allows the rough lines to draw atmospheric air rather than oil from the Alcatel pump. An oil trap ahead of the chamber helps to make the system fool-proof.

Substrate heating can be accomplished via a Neocera heater which can be removed with the substrate/film so that another dimension can be added to the combinatorial experiment. Annealing the sample during analysis will help to zero in on the desired deposition conditions. A low deposition temperature (substrate) is desired for energy savings and when multiple layers are to be deposited on one substrate where one layer may phase separate at high temperature.

Rf magnetron sputtering will be used to deposit ZnO:Al made p-type by nitrogen incorporation. First deposition target materials will be Process Material, Inc., ZnO (purity, 2" diameter x 0.125" thickness), Al (99.999% pure, 1" diameter, 0.125" thickness) and Prax Air nitrogen gas (purity). Evacuation will be achieved by rough pumping with an Alcatel SpectraVac to approximately 200 motor; further pumping will be done using a Ebara helium cryopump to approximately10^{-7} torr. Nitrogen gas will be fed at a pressure of approximately 40 mtorr. Substrate to target distance is anticipated to be 8 cm., the Al: 2N ratio will be maintained as much as possible by monitoring the MKS MFC readouts and nitrogen pressure from the ion gauge.

Analysis Setup

The components of the analysis setup are: Labview software, an Ocean Optics Inc. (OOI) OOIBase32 software package with an OOI S2000 spectrophotometer and reflective and transmissive fiber optics, a Neocera substrate heater, an x-y motion stage and controller (figure 5) and Igor, a graphical analysis package. The analysis begins once a film is deposited. The heater/substrate base will be removed from the sputtering chamber and set in place on the motion stage. Specific run parameters can be entered into Labview and scanning of, e.g., 100 grid points on a two inch square substrate can be initiated. Data from each grid point will be downloaded into Igor. By Igor's graphical analysis, film (TCO) parameters such as film thickness and estimates of the band gap can be compiled. The desired properties can then be correlated with composition. Subsequent deposition will be in a much narrower compositional range so that the ideal TCO composition/properties can be isolated.

Outlook

Because the vacuum system must still be leak-checked, no films have been deposited. Assuming targets of ZnO and Al are used in a nitrogen atmosphere, rf magnetron sputtering will hopefully produce a viable p-type semiconductor in the 2% Al / 4% N_2 compositional range. The Al composition of the film is expected to vary from nearly 0% Al to 10% Al from side to side. A separate run of ZnO without the Al target in a nitrogen atmosphere may reveal that the aluminum is/is not necessary to hold on to the nitrogen. ZnO as n-type will also be optimized by studying the effect of oxygen partial pressure on the oxygen vacancies.

NREL has produced p-type $CuAlO_2$ and $SrCu_2O_2$ by PLD. The deposition conditions and properties for each: [insert table]. The $SrCu_2O_2$ values indicate that this material is worthy of further research while the difficulty in $CuAlO_2$ fabrication and low temperature phase separation make it less viable.

The combinatorial approach to materials processing and analysis is becoming ever more essential with the frequent employment of ternary and quaternary systems. In conjunction with material complexity, other variables such as annealing/heating during analysis add new dimensions to the phase space. Where many variations must be investigated, the deposition gradients may allow for several hypotheses to be tested by analysis of one combinatorial sample. Using multiple source, rf magnetron sputtering and near-real-time spectrophotometry to determine ideal ternary TCO compositions is a prime example of the application of combinatorial synthesis and analysis.

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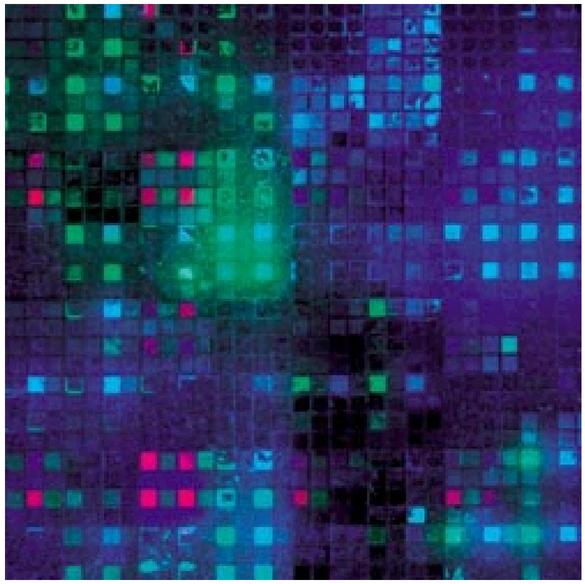

Figure 1. A deposited library of phosphors from LBNL. In order to demonstrate the power of a combinatorial approach, imagine how long it would take to find a specific set of property values and corresponding composition (e.g., the red phosphors) by linear experimentation. By using parallel experimentation, i.e., a combinatorial synthesis, one library can contain a very wide rang of compositions to be tested.

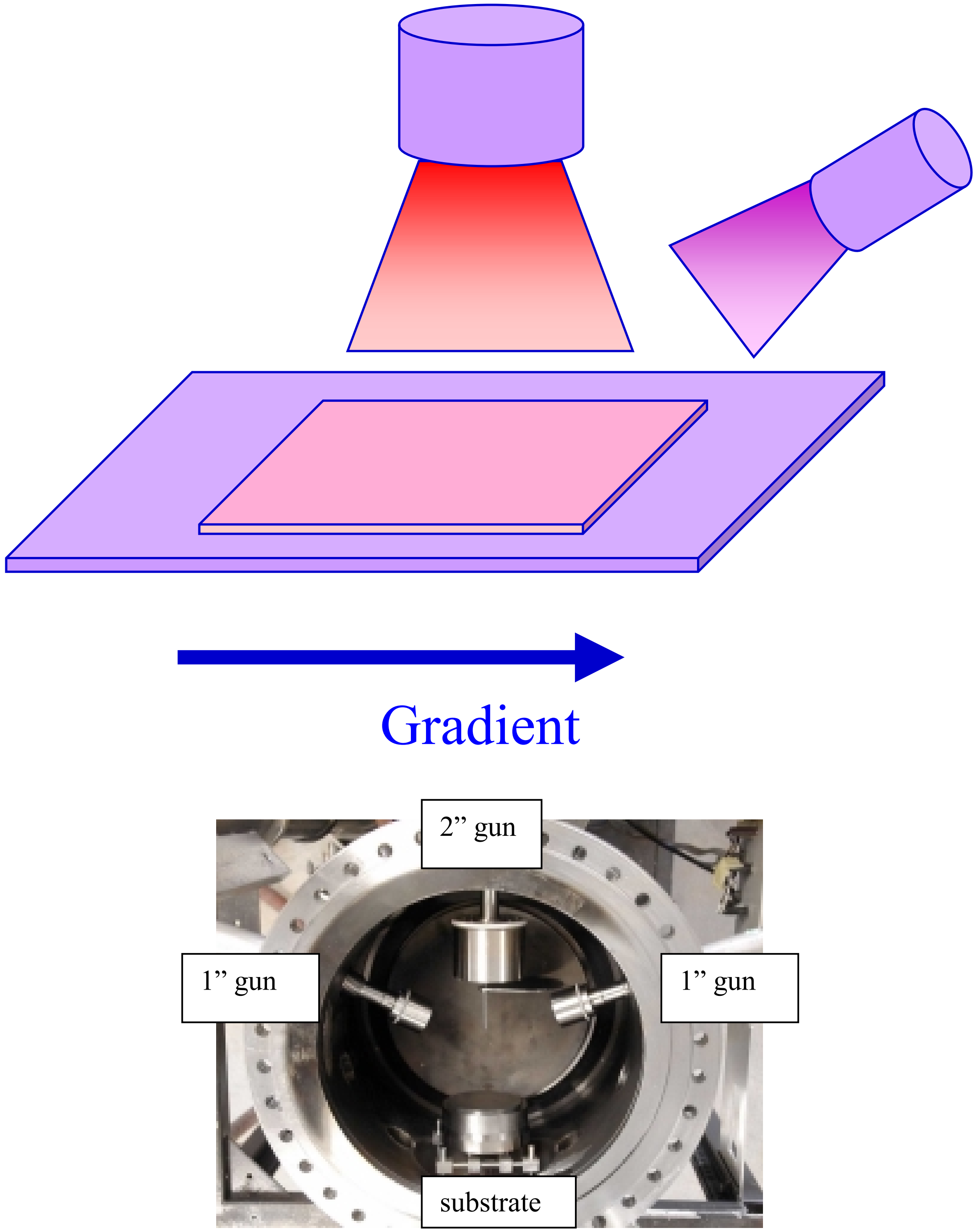

Figure 2. Combinatorial synthesis for a sputtering chamber. Compositional gradients are grown into the sample because of the oblique angle of the one-inch guns.

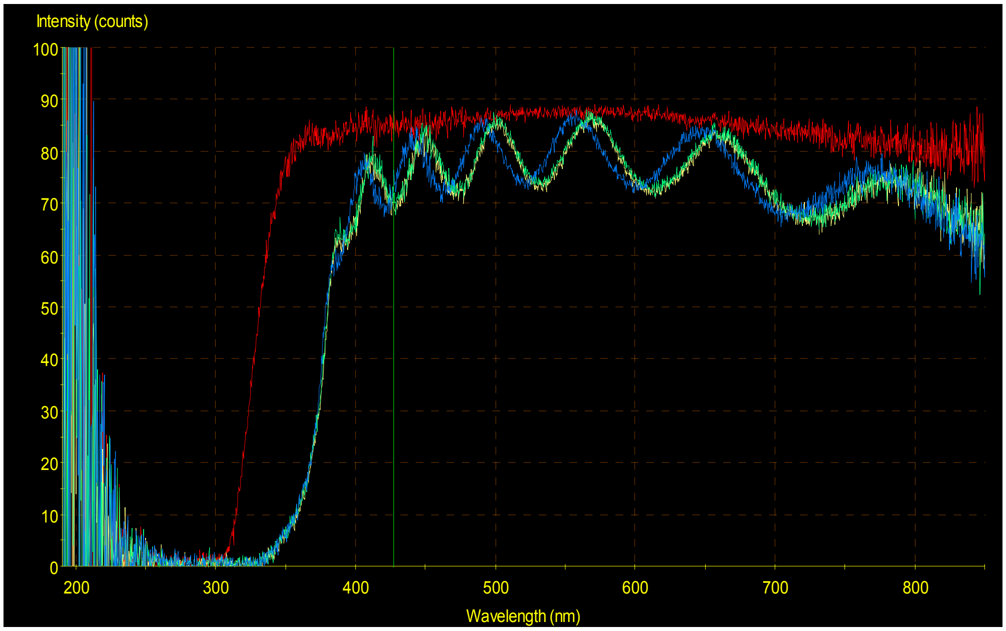

Figure 3. Two different points on a ZnO:Al sample TCO are represented by the blue and green spectra. The red spectrum is the 7059 glass substrate. These transmission spectra were taken using an Ocean Optics spectrophotometer coupled with fiber optic probe. Spectra can be taken in near-real-time. This figure hints at the volume of data that could be generated by scanning a deposition library.

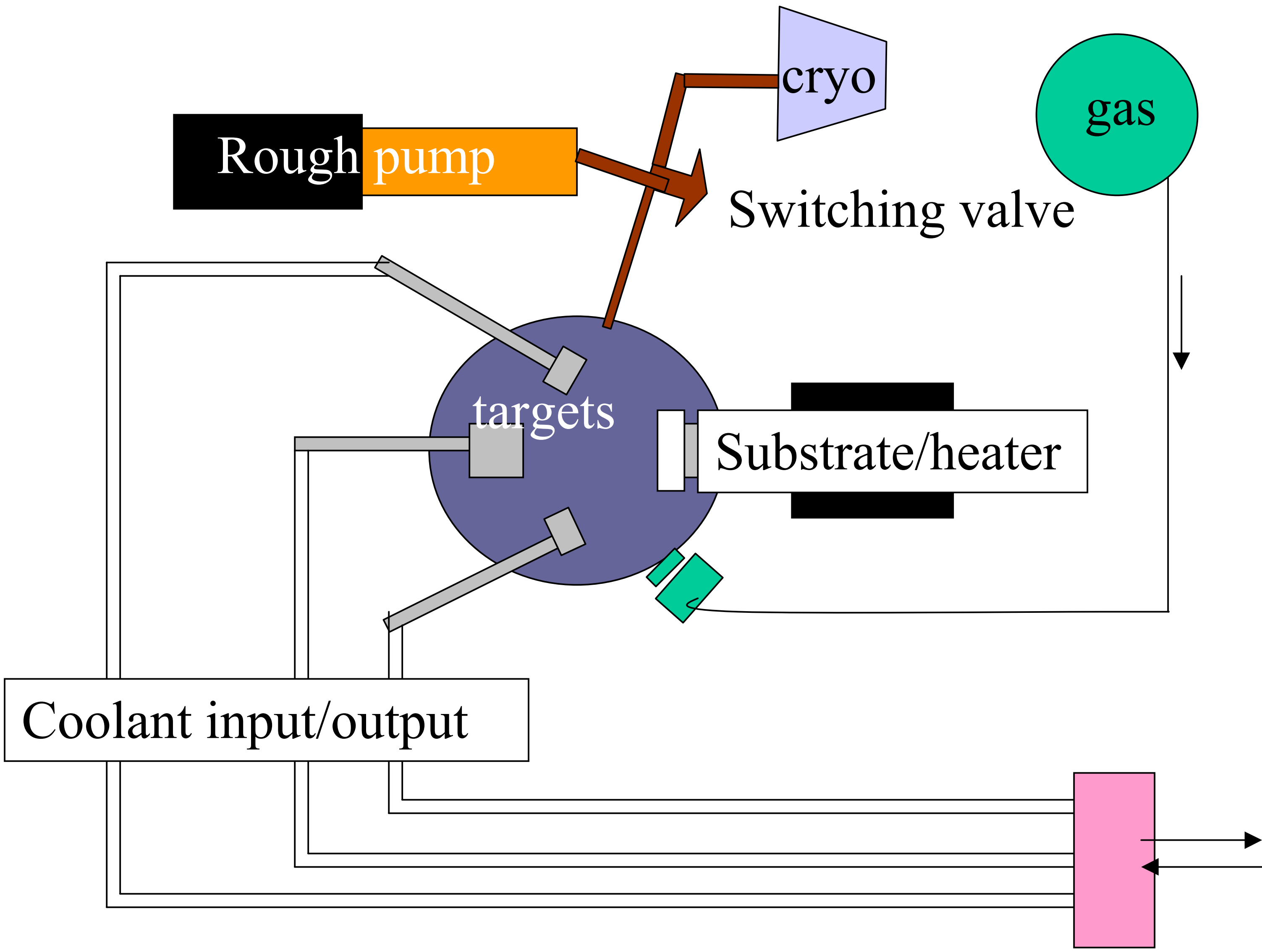

Figure 4. Sputtering support systems: cooling, vacuum, and gas.

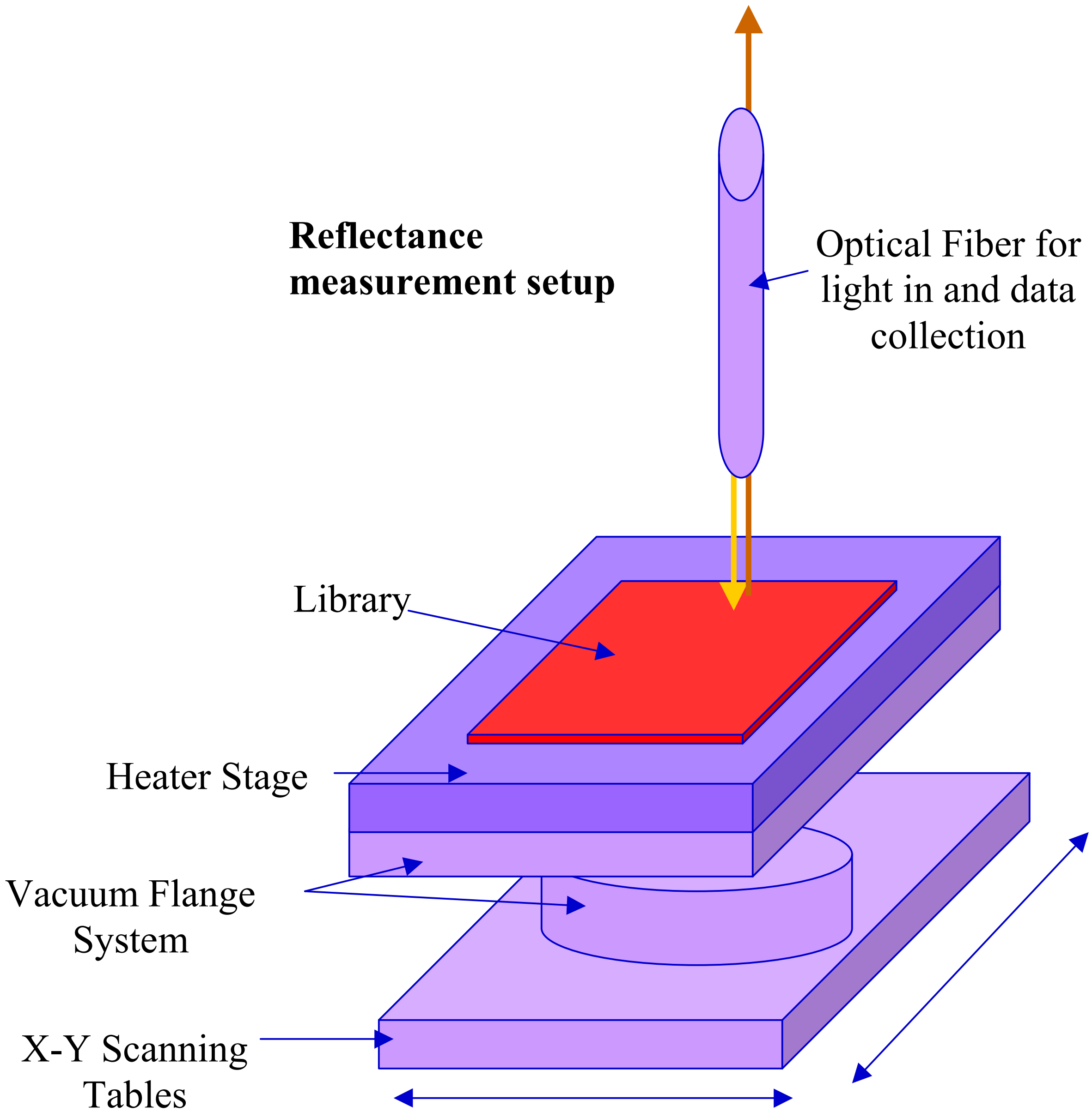

Figure 5. Combinatorial analysis for this system consists of a scanning table, substrate heater for annealing (adding a dimension to phase space), and a fiber optic probe connected to a near-real-time spectrophotometer. The system will be set up to take 100 spectra in a rastering fashion from a two-inch sample. This could plausibly be done in under 30 minutes. Data would be downloaded to a graphical analysis package after each spectra is taken.